

CO₂ Adsorption Techniques On High Surface Area Activated Carbons.

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1. INTRODUCTION

For years the subject of CO₂ adsorption on activated carbons has been both challenged and supported. The question remains whether or not CO₂ is a valid adsorbate for characterizing pore structures of activated carbons. The predominance of nitrogen adsorption as a routine experimental technique for BET surface area approximations has more or less overshadowed the limitations of this technique in terms of activated diffusion phenomena[1]. As a result, it is thought that nitrogen adsorption at 77K generally underestimates the surface area of coals[1]. In some super-activated carbons, CO₂ is an attractive adsorbate for characterization due to its small molecular diameter and it's access to supermicropores. Although CO₂ adsorption models are not completely understood, for particular cases in which N₂ adsorption may be problematic or inconclusive, CO₂ adsorption may offer additional pore structure information.

The purpose of this communication is to address the concept of CO₂ adsorption phenomena experimentally and conceptually. Experimental data are compared for CO₂ adsorbed onto very high surface area activated carbons. From this information, optimal experimental conditions are theorized on the basis of ease and understanding. It is hoped that an adsorption procedure involving the benefits of N₂ and CO₂ together will provide insight into the pore structures of very high surface area activated carbons.

2. EXPERIMENTAL

Materials used:

Two activated carbons were used in the experiments; they were supplied by Amoco Research and Development, and Norit N.V. Activated Carbon. They are classified as Amoco Super-A and Norit A-8982. The surface areas, as measured by nitrogen BET method[2], were 1500-1800 m²/g for Norit A-8982 and 2500-2800 m²/g for Amoco Super-A.

Experimental methods:

Adsorption analysis was performed on a Coulter Omnisorp 100CX Automated Gas Sorption System. Approximately 0.25 grams of sample was weighed prior to outgassing. All samples were outgassed at 250°C and sealed under vacuum prior to

analysis. Static volumetric mode was used for all CO₂ and N₂ adsorption measurements. N₂ was adsorbed at 77K in the relative pressure range (P/P_0) of 0.001 to 0.98. CO₂ was adsorbed at three different temperatures and relative pressure ranges(P/P_0) as follows:

195K: 0.0001 to 0.48
273K: 0.0001 to 0.027
298K: 0.0002 to 0.015

CO₂ saturation vapor pressures for each temperature were taken as follows:

195K: 1,410 torr[3]
273K: 26,068 torr
298K: 45,041 torr

Molecular diameters used for N₂ and CO₂ were 3.64 and 3.3 angstroms, respectively. All surface areas were calculated from the BET equation[2] and pore volumes were approximated using the Dubinin-Radushkevich equation[4].

3. RESULTS AND DISCUSSION

The CO₂ adsorption isotherms for the A-8982 and the Amoco Super-A carbons at 195K, 273K, and 298K are plotted in Figures 1 and 3, respectively. Upon initial examination for the Norit carbon, the CO₂ uptake at 195K in this low pressure region is markedly higher than in the other two temperature cases. At 273K and 298K, the isotherms are virtually identical with very little deviation in CO₂ uptake. The Amoco Super-A carbon exhibits similar characteristics in this region but with a noticeable difference in the 273K and 298K temperature cases. These results suggest that, at 195K, complete micropore filling may occur giving higher potential for CO₂ adsorption. It is likely that incomplete micropore filling occurs at temperatures of 273-298K since the saturation vapor pressure of CO₂ is extremely sensitive to temperature changes and is very high. However, it seems reasonable to assume that, at 195K, a better estimate of internal pore uptake can be obtained.

The CO₂ DR plots for A-8982 and Amoco Super-A are indicated in Figures 2 and 4, respectively. In estimating pore volumes, a comparable range for each temperature was taken for extrapolation to the y-axis. The pore volumes are as follows:

Norit 195K = 1.22 cc/g	Amoco 195K = 2.00 cc/g
Norit 273K = 0.93 cc/g	Amoco 273K = 1.40 cc/g
Norit 298K = 1.09 cc/g	Amoco 298K = 1.64 cc/g

At an adsorption temperature of 195K the pore volumes are the highest which relates to the increased uptake observed in the adsorption isotherms in figures 1 and 3. Pore volume calculations from N₂ adsorption are slightly less than the 195K CO₂ case but higher than 273K and 298K CO₂ cases. Results obtained from BET surface

area calculations for the 195K CO₂ case yield higher surface areas than N₂ BET estimates.

4. CONCLUSIONS

CO₂ adsorption at 195K appears to be a valid technique for approximating pore volumes of high surface area activated carbons if complete micropore filling is assumed. Experimentally, due to instrumental limits, a larger relative pressure range can be analysed for 195K due to the temperature and vapor pressure sensitivities present at 273K and 298K. Because of this fact, CO₂ and N₂ surface areas can be compared. Since the relative pressure ranges for 273K and 298K are so low, (maximum $p/p_0 = 0.02-0.03$), the micropore filling is incomplete, giving pore volumes that are underestimated. Although a strict comparison between CO₂ and N₂ needs to be investigated further, molecular size differences may still give some insight on the possible presence of any super microporosity.

5. REFERENCES

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3. H. Marsh, D. Crawford, T.M. O'Grady, and A. Wennerberg, Carbon Vol. 20 No 5, pp. 419-426, 1982.
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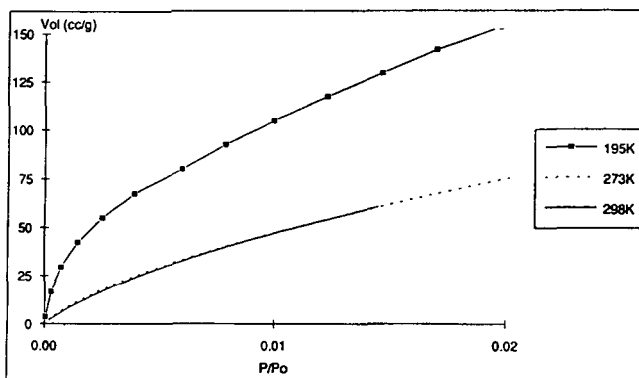


Fig. 1. CO₂ adsorption isotherms on Norit activated carbon at 195K, 273K, and 298K.

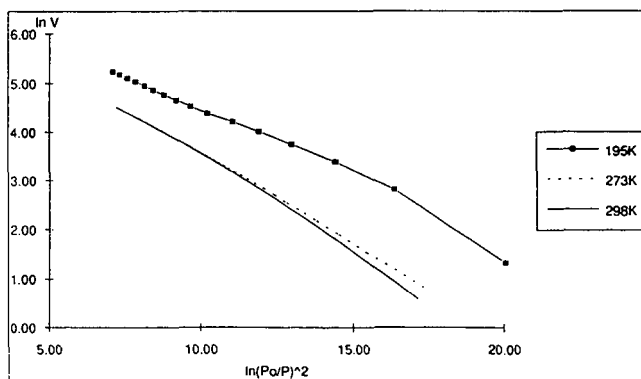


Fig. 2. CO₂ DR plots corresponding to isotherms in Fig. 1.

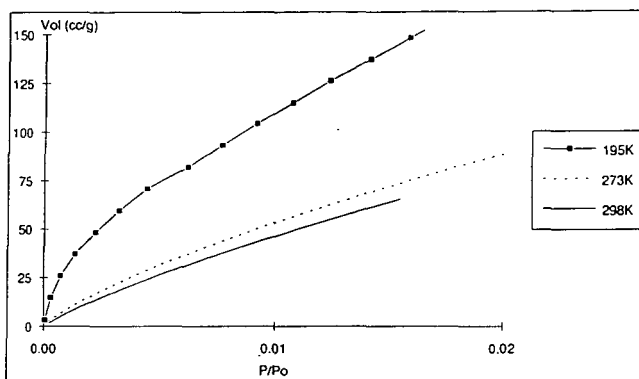


Fig. 3. CO₂ adsorption isotherms on Amoco Super-A activated carbon at 195K, 273K, and 298K.

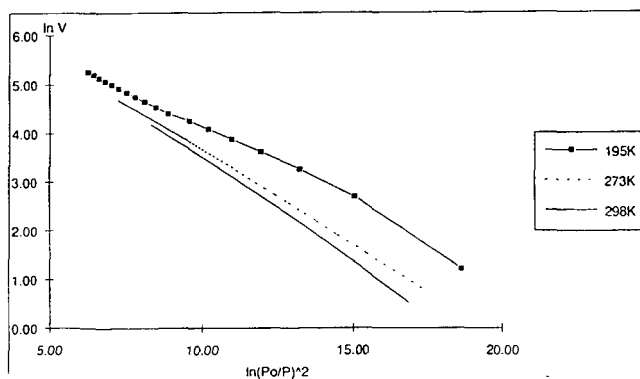


Fig. 4. CO₂ DR plots corresponding to isotherms in Fig. 3.